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(54) INK COMPOSITION FOR OZONE DETECTION AND OZONE INDICATOR

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an ink compsn. which can detect ozone easily and conveniently without fail by compounding an anthraquinone dye having at least one kind of amino group selected from prim- and sec-amino groups with a cationic surfactant of a quaternary ammonium salt type.

SOLUTION: Alkyltrimethylammonium salts and dialkyldimethylammonium salts are esp. pref. cationic surfactants of quaternary ammonium salt types. Though this compsn. can be used as it is, it may be supported by a substrate, by coating or impregnation, before being used. This compsn. is suitably used as a color changing layer of an ozone indicator. The indicator is prepd. by forming a color changing layer comprising the ink compsn. for ozone detection and a color nonchanging layer comprising an ink not changing in color by ozone on a substrate so that at least a part of the color changing layer is exposed to an ozone atmosphere.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the design printed using the ink for ozone detection in the example 4.

[Drawing 2] It is drawing showing the design usually printed using color ink in the example 4.

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DRAWINGS

[Drawing 1]



[Drawing 2]



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the ink constituent for ozone detection, and the ozone indicator which used the constituent.
[0002]
[Description of the Prior Art] Since ozone is excellent in disinfectant [the] etc., it is used for sterilization and disinfection of food and instruments, the sterilization and disinfection in a fixed ambient atmosphere like the operating room of a hospital, or deodorization. On the other hand, toxicity of ozone is very strong, and since it also affects the body, a limitation is in the threshold limit value. On the other hand, in a photochemical smog forecast, the level of oxidants in atmospheric air serves as an important element.
[0003] For this reason, that detection approach is developed variously that an ozone level should be supervised. As the ozone (oxidant) detection approach in the former, discoloration by the reaction of a bottom type (1) is mainly used.
[0004]
[Formula 1]

$$KI \xrightarrow{(O)} I_2$$

[0005] The approach of measuring optically the discoloration degree which introduced the gas which contains ozone in a cadmium potassium solution, for example as the detection approach using this principle, and is proportional to the amount of the generated iodine with a colorimeter or the approach by the indicator tube simple type, the approach by the cadmium potassium-starch paper, etc. are learned conventionally.
[0006] However, by the above-mentioned optical measuring method, equipment itself is dramatically expensive, and in measuring especially two or more places, there is a problem in respect of costs and actuation. Moreover, in an indicator tube, in addition, a simple thing is more expensive than optical means, and whenever it moreover measures, it is necessary to attract an oxidant with hand control or automatic. Although a cadmium potassium-starch paper is cheap and simple, since sensibility is low, it is not applicable to detection of the low-concentration oxidant of hundreds of or less ppb as a matter of fact.
[0007] The ozone detecting element containing a triphenylmethane color system leuco and an acid stabilizer is proposed about this (JP,62-291564,A). This detects ozone using the coupling by oxidation of a color leuco. According to this technique, it becomes detectable [ozone] in the condition of having dried without needing actuation of carrying out humidity with moisture.
[0008]
[Problem(s) to be Solved by the Invention] However, the triphenylmethane color system leuco itself tends to oxidize in air, for this reason, it is necessary to add the acid of the amount of specification, and a

stabilizer as an indispensable component, and there is room which should improve in addition in fields, such as simple nature, shelf life (stability), and precision, with the above-mentioned conventional technique.

[0009] Thus, also in which conventional technique, the actual condition is that the approach of detecting ozone that it is simple and certainly is not yet developed.

[0010] Therefore, this invention sets it as the main objects to offer the ingredient which can detect ozone simpler and certainly.

[0011]

[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of the trouble of the conventional technique, this invention person finds out having the function in which the ink constituent containing a specific component can detect ozone effectively, and came to complete this invention at last.

[0012] That is, this invention relates to the ink constituent for ozone detection containing the cation system surfactant of the anthraquinone system color which has at least one sort of amino groups of the first amino group and the second amino group, and a quarternary-ammonium-salt mold.

[0013] This invention the discoloration layer which consists of an ink constituent for the ** above-mentioned ozone detection on a base material Furthermore, at least one layer, ** Start the ozone indicator characterized by forming the discoloration layer and the non-discoloring layer so that it may have at least one layer and a part or all of at least one discoloration layer may be exposed to an ozone ambient atmosphere in the non-discoloring layer which consists of ink which is not discolored by ozone.

[0014]

[Embodiment of the Invention] The anthraquinone system color used by this invention makes anthraquinone a basic frame, especially as long as it has at least one sort of amino groups of the first amino group and the second amino group, it is not restricted, but a well-known anthraquinone system disperse dye etc. can be used for it. You may have the above-mentioned amino group two or more, and they may differ of the same kind [these] or mutually. As such an anthraquinone system color, for example 1,4-diaminoanthraquinone (C. I.Disperse Violet 1), 1-amino-4-hydroxy-2-methoxy anthraquinone (C. I.Disperse Red 4), 1-amino-4-methylamino anthraquinone (C. I.Disperse Violet 4), 1, 4-diamino-2-methoxy anthraquinone (C. I.Disperse Red 11), 1-amino-2-methylanthraquinone (C. I.DisperseOrange 11), 1-amino-4-hydroxy anthraquinone (C. I.Disperse Red15), 1, 4, 5, 8-tetra-aminoanthraquinone (C. I.Disperse Blue 1), 1, and 4-diamino-5-nitro anthraquinone (C. I.DisperseViolet 8) etc. can be mentioned (the inside of a parenthesis is a color number). In addition to this C.I.Solvent Blue14, C.I.Solvent Blue 63, C.I.Solvent Violet 13, C.I.Solvent Violet 14, and C.I.Solvent Red 52 and C.I.Solvent Red 114, C.I.Vat Blue 21, and C.I.Vat Blue 30 and C.I.Vat Violet 15, C.I.Vat Violet 17, and C.I.Vat Red 19, C.I.Vat Red 28, C.I.Acid Blue 23, C.I.Acid Blue 80, C.I.Acid Violet 43, C.I.Acid Violet48, and C.I.Acid Red 81, C.I.Acid Red 83, C.I.Reactive Blue 4, C.I.ReactiveBlue 19, and C.I.Disperse Blue 7 etc. -- ****** -- the color known can also be used. These anthraquinone system colors are independent, or can be used together two or more sorts. the inside of these anthraquinone system color -- C.I Disperse Blue 7 and C.I Disperse Violet 1 etc. -- it is desirable. Moreover, the detection sensibility of ozone is also controllable by this invention by changing the classes (molecular structure etc.) of these anthraquinone system colors.

[0015] Especially as a cation system surface active agent (only henceforth a "cation system surface active agent") of a quarternary-ammonium-salt mold, it cannot be restricted, but alkyl ammonium salt can usually be used, and this can also use a commercial item. Moreover, these can be used by one sort or two sorts or more. In this invention, the more excellent discoloration effectiveness can be acquired by using these cation system surfactant together with said anthraquinone system color.

[0016] Also in these cation system surface active agent, an alkyl trimethylammonium salt, a dialkyl dimethylannmonium salt, etc. are desirable. Chlorination coconut alkyl trimethylammonium, chlorination beef tallow alkyl trimethylammonium, chlorination behenyl trimethylammonium, chlorination dodecyl trimethylammonium, chlorination hexadecyl trimethylammonium, chlorination

lauryl trimethylammonium, chlorination octadecyl trimethylammonium, chlorination dioctyl dimethylannmonium, chlorination distearyldimethylbenzylammonium, chlorination alkyl benzyl dimethylannmonium, etc. are mentioned, and, specifically, especially chlorination lauryl trimethylammonium is desirable.

[0017] Although the ink constituent of this invention can be used as long as the above-mentioned anthraquinone system color and the cation system surface active agent contain, it can blend suitably the component used for well-known ink constituents, such as a resin system binder, an extending agent, and a solvent, if needed.

[0018] The well-known resinous principle used for the ink constituents the object for a note, for printing, etc. is [that what is necessary is just to choose suitably as a resin system binder according to the class of base material etc.] employable as it is. Specifically, maleic resin, amide resin, ketone resin, alkylphenol resin, rosin modified resin, a polyvinyl butyral, a polyvinyl pyrrolidone, cellulose type resin, etc. can be mentioned.

[0019] Especially as an extending agent, it is not restricted, for example, a bentonite, the activated clay, an aluminum oxide, silica gel, etc. can be mentioned. In addition, the ingredient known as a well-known extender can be used. Also in this, a porous thing is desirable and especially silica gel is more desirable. By adding these extending agents, detection sensibility can mainly be adjusted.

[0020] As a solvent which can be used by this invention, if it is the solvent used for the ink constituents the object for printing, for a note, etc., all can usually be used. For example, what is necessary is to be able to use various solvents, such as an alcoholic system, an ester system, an ether system, a ketone system, and a hydrocarbon system, and just to choose suitably according to the solubility of the color to be used and a resin system binder etc.

[0021] The anthraquinone system color which uses the rate in the case of blending these all, Although what is necessary is just to set up suitably according to the class of cation system surfactant etc., an application, etc. Usually, after considering as 0.05 - 10 % of the weight (preferably 0.1 - 1 % of the weight) of anthraquinone system colors in this invention ink constituent, and 0.2 - 30 % of the weight (preferably 0.5 - 10 % of the weight) of cation system surfactants What is necessary is for 50 or less (preferably 5 - 35 % of the weight) % of the weight of resin system binders, 1 - 30 % of the weight (preferably 2 - 20 % of the weight) of extending agents etc., etc. just to adjust.

[0022] In this case, when coloring becomes inadequate when an anthraquinone system color is less than 0.05 % of the weight, and it is hard to identify the color difference before and behind discoloration and it exceeds 10 % of the weight, there is a possibility that discoloration may become not clear. When there are too few resin system binders, in case this invention ink constituent is printed and used for a base material, when the adhesion to a base material becomes imperfection and exceeds 50 % of the weight, good printing nature is no longer obtained. In not acquiring discoloration effectiveness (color difference) sufficient when a cation system surfactant is less than 0.2 % of the weight and exceeding 30 % of the weight, a possibility of causing trouble is in formation of a paint film. Moreover, also when there are too many extending agents, good printing nature is no longer obtained. Therefore, if each component is blended within the limits of the above, when printing and using it especially for a base material, coloring, discoloration, etc. become clear and can acquire moreover more good printing nature and adhesion.

[0023] What is necessary is to blend each [these] component being simultaneous or one by one, and just to mix it to homogeneity using well-known agitators, such as a homogenizer and a desolver. For example, what is necessary is to blend an anthraquinone system color, a cation system surface active agent, a resin system binder, an extending agent, etc. with a solvent in order first, and just to mix and stir.

[0024] Although it can also be used as it is, it can also be used by performing spreading of an ink constituent, impregnation, etc. to a base material if needed, making a base material able to support this invention ink constituent. What is necessary is not to be restricted, for example, to be able to apply especially as a base material, to either paper, a woody ingredient, plastics, a metal and an alloy, the ceramics cement concrete or such composite material, and just to choose suitably according to a service

space, an application, etc.
[0025] Especially the ink constituent for ozone detection of this invention can be used suitable also for the ozone indicator which used this for the discoloration layer. That is, the ozone indicator of this invention is characterized by forming the discoloration layer and the non-discoloring layer so that it may have at least one layer and a part or all of at least one discoloration layer may be exposed to an ozone ambient atmosphere in the non-discoloring layer which consists of ink which does not discolor the discoloration layer which consists of an ink constituent for ozone detection of ** above on a base material by at least one layer and ** ozone.
[0026] As a base material used with the ozone indicator of this invention, especially as long as a discoloration layer or a non-discoloring layer can be formed, it is not restricted, but the same thing as said base material can be used.
[0027] On the other hand, any ink can be used for the non-discoloring layer in the ozone indicator of this invention unless it discolors by ozone. as such ink -- marketing -- color ink can also usually be used. For example, water color ink, oil based ink, non-solvent mold ink, etc. can be used. Moreover, when printing, according to the printing approach, well-known letterpress ink, rotogravure ink, screen ink, offset ink, etc. can be used properly suitably. These ink may be used independently as they are, or may mix and tone two or more sorts. Moreover, the components (for example, a resin system binder, an extending agent, a solvent, etc.) blended with the well-known ink constituent may be contained in the ink in a non-discoloring layer.
[0028] Formation of the discoloration layer in this invention and a non-discoloring layer can be performed according to the well-known printing approaches, such as silk screen printing, gravure, offset printing, Toppan Printing, and flexographic printing, using each ink. What is necessary is not to restrict especially the sequence of printing of a discoloration layer and a non-discoloring layer, but just to choose it suitably according to the design to print.
[0029] In this invention ozone indicator, you may form a discoloration layer and one layer of non-discoloring layers at a time, respectively, or they may carry out the laminating of two or more layers, respectively. Moreover, the laminating of discoloration layers or the non-discoloring layers may be carried out. In this case, you may be a presentation which is different even if discoloration layers are the same presentations mutually. You may be a presentation which similarly is different even if non-discoloring layers are the same presentations mutually.
[0030] Furthermore, a discoloration layer and a non-discoloring layer may be formed all over a base material or each class, or may be formed selectively. In order to secure discoloration of a discoloration layer especially by this invention in these cases, a discoloration layer and a non-discoloring layer are formed so that a part or all of at least one discoloration layer may be exposed to an ozone ambient atmosphere.
[0031] In this invention, as long as existence of ozone is discriminable, a discoloration layer and a non-discoloring layer can be formed, or it can also form so that the color difference of a discoloration layer and a non-discoloring layer cannot be identified without discoloration of a discoloration layer and the color difference of a discoloration layer and a non-discoloring layer may not arise for the first time by discoloration. It is desirable to form a discoloration layer and a non-discoloring layer so that the color difference of a discoloration layer and a non-discoloring layer can be especially identified only after discoloring.
[0032] What is necessary is just to form a discoloration layer and a non-discoloring layer so that at least one of an alphabetic character, a pattern, and the notations cannot be identified without discoloration of for example, a discoloration layer in enabling it to identify the color difference. In this invention, an alphabetic character, a pattern, and a notation include all the information that tells discoloration (namely, existence of ozone). What is necessary is just to design these alphabetic characters etc. suitably according to the purpose of use etc.
[0033] Moreover, although it is good also as a color which is mutually different in the discoloration layer and the non-discoloring layer before discoloration, especially both are substantially made into the same color, and you may enable it to identify the color difference (contrast) of a discoloration layer and

a non-discoloring layer for the first time after discoloration.
[0034] In this invention ozone indicator, a discoloration layer and a non-discoloring layer may be formed so that a discoloration layer and a non-discoloring layer may not lap. Thereby, the amount of ink to be used can also be saved.
[0035] Furthermore, in this invention, a discoloration layer or a non-discoloring layer may be further formed on one [at least] layer of a discoloration layer and a non-discoloring layer. For example, if the discoloration layer which has still more nearly another design from the layer (it is called "discoloration-a non-discoloring layer") in which the discoloration layer and the non-discoloring layer were formed is formed so that a discoloration layer and a non-discoloring layer may not lap Since the borderline of the discoloration layer in discoloration-a non-discoloring layer and a non-discoloring layer changes into the condition of not being substantially discriminable, the more excellent appearance can be attained.
[0036]
[Effect of the Invention] (1) If ozone is contacted, even if the ink constituent for ozone detection of this invention will be in the condition dried substantially, discolor or decolorize it, and also with the naked eye, it can detect existence of ozone easily, and is excellent in detection precision (selectivity), sensibility, stability, etc. Since especially both the cation system surfactants of a quarternary-ammonium-salt mold are blended, it is possible for allochroic [more excellent] to be acquired and to also detect lower-concentration ozone certainly. Depending on conditions, the low-concentration ozone of 0.03 ppm is also detectable, for example.
[0037] Furthermore, it is possible to control detection sensibility, a discoloration rate, etc. by the constituent of this invention freely by changing the class and the blending ratio of coal of a component, such as an anthraquinone system color.
[0038] With this invention ink constituent, by blending a resin system binder etc., it can use also as the object for printing, the object for a note, and ink for stamps, and can use in the condition of having applied on base materials, such as paper and a film. For this reason, if several sorts of paint films of this invention ink constituent discolored or decolorized for the first time, for example by the fixed ozone level are made to form on a base material, it can use as a simple ozone indicator.
[0039] (2) Since the ozone indicator of this invention consists of combination of a specific discoloration layer and a non-discoloring layer, it can identify discoloration certainly and, thereby, can detect existence of ozone easily. Moreover, since a tooth space cannot be taken, either but flexible nature can moreover also be given by selection of a base material if it is made the shape for example, of a sheet, or tabular as the whole configuration, it becomes possible to install anywhere.
[0040] And by combining a discoloration layer and a non-discoloring layer suitably, the pattern embraced in activity eye, an alphabetic character, a notation, etc. can be expressed, and it can apply to a broad application from the ability of the outstanding design nature to also be given.
[0041] Since the ink constituent for ozone detection which contains the cation system surfactant of a quarternary-ammonium-salt mold as an indispensable component is use especially for this invention ozone IJIKETA as a discoloration layer , even if it is in the condition dried substantially , it discolors in response to ozone and an effectiveness target , and it demonstrates an outstanding detection precision (selectivity) , sensibility , stability , etc. , and , also with the naked eye , can detect existence of ozone easily . Furthermore, it is also possible by changing the class and the blending ratio of coal of a component, such as the above-mentioned cation system surfactant and an extending agent, to be able to control detection sensibility, a discoloration rate, etc. freely and to detect an ozone level quantitatively.
[0042]
[Example] Hereafter, an example and the example of a comparison are shown and the description of this invention is clarified further.
[0043] The example 1 anthraquinone system disperse dye ("MIKETON fast red violet R" Mitsui Toatsu Chemicals, Inc. make) 0.20 weight section, As a resin system binder, the ethyl cellulose system resin ("ethocell 10" Dow Chemical Co. make) 7.35 weight section, The silica gel (product made from "Aerosil R-972" Japan Aerosil) 9.80 weight section, The ethylcellosolve ("C HOZORU MG" NIPPON SHOKUBAI Co., Ltd. make) 80.69 weight section is mixed with an agitator to homogeneity as a cation

system surface active agent as the chlorination coconut alkyl trimethylammonium (product made from "CA-2150" NIKKOL) 1.96 weight section, and a solvent. this invention ink constituent was prepared.
[0044] this invention ink constituent was prepared like the example 1 except having used the chlorination lauryl trimethylammonium ("Kohtamin 24P" Kao Corp. make) 1.96 weight section as an example 2 cation system surface active agent.
[0045] The ink constituent was prepared like the example 1 except not using an example of comparison 1 cation system surfactant. However, only the part of a cation system surface active agent filled up solvent ethylcellosolve, and was made into the solvent 82.65 weight section.
[0046] The example 3 anthraquinone system disperse dye ("MIKETON fast TAKOIZU blue" Mitsui Toatsu Chemicals, Inc. make) 0.24 weight section, As a resin system binder, the ethyl cellulose system resin ("ethocell 10" Dow Chemical Co. make) 9.15 weight section, The silica gel (product made from "Aerosil R-972" Japan Aerosil) 12.20 weight section, The ethylcellosolve ("C HOZORU MG" NIPPON SHOKUBAI Co., Ltd. make) 75.97 weight section is mixed with an agitator to homogeneity as a cation system surface active agent as the chlorination hexadecyl trimethylammonium ("cation PB-40" Nippon Oil & Fats Co., Ltd. make) 2.44 weight section and a solvent. this invention ink constituent was prepared.
[0047] The ink constituent was prepared like the example 1 except not using an example of comparison 2 cation system surfactant. However, only the part of a cation system surface active agent filled up solvent ethylcellosolve, and was made into the solvent 78.41 weight section.
[0048] It investigated allochroic [in each ink constituent obtained in example of trial 1 examples 1-3, and the examples 1-2 of a comparison].
[0049] It printed in the Kent paper by silk screen printing (150 meshes) using each ink constituent. When the obtained print was exposed for about 15 minutes into the 0.3 ppm ozone ambient atmosphere, signs that the printed color was faded or decolorized were observed with the naked eye. The discoloration condition after discoloration was investigated by the color difference (deltaE) with exposure before (before discoloration). The result is shown in a table 1.
[0050]
[A table 1]

	色差ΔE
実施例1	43.2
実施例2	48.8
比較例1	28
実施例3	45.6
比較例2	26.1

[0051] In the examples 1-2 of a comparison, since the color difference is small, the result of a table 1 shows that the color difference is large and there is little color remainder by the examples 1-3 to a thing with the large color remainder after discoloration. This shows that it can detect it as 0.3 ppm certainly even if an ozone level is low in this invention ink constituent.
[0052] The ozone indicator was produced using the ink constituent for ozone detection prepared in the example 4 example 1. On the other hand, the common color ink used in a non-discoloring layer was toned. The white "concentrated 061-ink a" 60.6 weight section, the purple "082-ink A" 6.1 weight section, and the medium ink "medium" 33.3 weight section (all are the products made from "auction call JM series (mat type)" empire ink) were mixed, and color ink (thin purple) was usually obtained.
[0053] The alphabetic character design "finishing [deodorization] (NUKI alphabetic character)" which uses the ink for ozone detection and is shown in drawing 1 was printed in the Kent paper by silk screen printing (150 meshes), and the discoloration layer was formed in it. Subsequently, the alphabetic character design "finishing [deodorization]" usually shown in drawing 2 using color ink was printed by silk screen printing (300 meshes), the non-discoloring layer was formed, and the whole surface obtained the indicator of thin purple so that it might not lap with a discoloration layer. In addition, in this

invention, it is good about the design shown in drawing 1 and drawing 2 also considering which as the ink for ozone detection, or common color ink. Moreover, whichever also of the sequence of printing of both designs may be the point.

[0054] When the obtained indicator was left for about 15 minutes in the ozone ambient atmosphere (ozone level: about 0.3 ppm), only the discoloration layer which consists of the above "finishing [deodorization] (NUKI alphabetic character)" decolorizes, and the "deodorized alphabetic character" of a non-discoloring layer could identify as an alphabetic character of thin purple for the first time according to the color difference.

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CLAIMS

[Claim(s)]
[Claim 1] The ink constituent for ozone detection containing the cation system surfactant of the anthraquinone system color which has at least one sort of amino groups of the first amino group and the second amino group, and a quarternary-ammonium-salt mold.
[Claim 2] The ink constituent for ozone detection according to claim 1 whose cation system surface active agent of a quarternary-ammonium-salt mold is an alkyl trimethylammonium salt.
[Claim 3] The ink constituent for ozone detection according to claim 1 or 2 which contains an extending agent further.
[Claim 4] The ink constituent for ozone detection according to claim 1 or 2 which contains a resin system binder further.
[Claim 5] a base material top -- ** -- the discoloration layer which consists of an ink constituent for ozone detection according to claim 1 to 4 with at least one layer ** The ozone indicator characterized by forming the discoloration layer and the non-discoloring layer so that it may have at least one layer and a part or all of at least one discoloration layer may be exposed to an ozone ambient atmosphere in the non-discoloring layer which consists of ink which is not discolored by ozone [claim 6] The ozone indicator according to claim 5 with which the discoloration layer and the non-discoloring layer are formed so that the color difference of a discoloration layer and a non-discoloring layer can be identified only after a discoloration layer discolors.
[Claim 7] The ozone indicator according to claim 5 with which the discoloration layer and the non-discoloring layer are formed so that at least one of an alphabetic character, a pattern, and the notations can be identified only after a discoloration layer discolors.
[Claim 8] The ozone indicator according to claim 6 or 7 whose discoloration layer and non-discoloring layer before discoloration are the same color substantially.
[Claim 9] The ozone indicator according to claim 5 to 8 with which the discoloration layer and the non-discoloring layer are formed so that a discoloration layer and a non-discoloring layer may not lap.
[Claim 10] The ozone indicator according to claim 5 to 9 with which the discoloration layer or the non-discoloring layer is further formed on one [at least] layer of a discoloration layer and a non-discoloring layer.

[Translation done.]